Comparison of the performance and EIS (electrochemical impedance spectroscopy) response of an activated PEMFC (proton exchange membrane fuel cell) under low and high thermal and pressure stresses

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ABSTRACT

In this study, it was demonstrated that membrane electrode assembly (MEA) conditioning at the low stress condition produces a higher performance compared to MEA conditioning under the high stress condition, although it needs more time to accomplish.

The maximum power density (MPD) of 1600 mW cm^{-2} was achieved by the MEA activated at low temperature and pressure (MEA-LTP) compared to the MEA activated at high temperature and pressure (MEA-HTP) in the same operating conditions, 1090 mW cm^{-2}, whiles the MEA structure of both cells was identical. MEA conditioning at the low stress condition enhances not only the fuel cell power but also its energy efficiency by 25%. Comparison of electrochemical impedance spectroscopy (EIS) responses of MEA-LTP and MEA-HTP indicated that an extension of the triple phase boundary occurred in MEA-LTP, which was consistent with the results of the MEA performance analysis.

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1. Introduction

The proton exchange membrane fuel cell (PEMFC) is a promising power source for portable electronic devices and residential uses due to its fast start-up, high efficiency, and stable performance [1,2]. The key component that determines the performance of a PEMFC is its membrane electrode assembly (MEA). The electrochemical reactions in the MEA do not fully occur during the initial operation and cause irreversible deterioration of the overall performance of the MEA [3]. An activation period is necessary to initiate the newly fabricated MEA in the PEMFC. The MEA activation provides different advantages, including the removal of impurities introduced during the process of manufacturing the MEA [4], activation of catalysts not participating in the reaction [5], creation of passages for reactants and products transportation to the catalyst site [3], and the hydration of Nafion presented in the membrane and electrode catalyst layer [6,7]. Therefore, during the MEA activation procedure, the membrane, diffusion, and catalyst layer experience strong changes in their properties.

Up to now, many studies have been conducted on MEA activation such as MEA activation mechanism investigation [8—12], the use of different activation procedures [13—16], and development of new methods for MEA or electrode activation [4,17—19] before or after cell assembly.

Although all mentioned strategies in the literature [13—19] accelerate MEA activation, the activation process is still a time-consuming process and remains one of the undeveloped challenges confronting PEMFC systems.

MEA activation not only takes up significant time, but also consumes a considerable amount of reactants, resulting in a high cost for operating the PEMFC. The quality and time of the MEA activation process are controlled by different parameters such as the MEA composition and making process [11], off/on line MEA conditioning [4], and the condition of MEA activation [12,18—20], especially cell temperature, reactants pressure and humidity; this last parameter is also controlled by gas pressure and temperature. Therefore, temperature and pressure of the MEA activation condition are very important factors that strongly affect the MEA performance and its activation time.

X. Z. Yuan et al. [12] found that high temperature was effective in obtaining a high performance; however, open circuit voltage (OCV)

relaxation and cycling steps were not very helpful in accelerating the MEA activation process. Indeed, a high cycling frequency reduced the MEA activation time, but it was soon followed by degradation. C. Yang et al. [18] introduced a three-step MEA activation procedure in conjunction with a stepped current profile. Activation temperature was not kept constant. The activation procedure was tested in time varying conditions at three different temperatures. The results showed that by varying MEA activation temperature in a time dependent way, the MEA performance was greatly improved. Z. Qi et al. [19] provided an effective and fast activation procedure by exposing the PEMFC to elevated temperature combined with the elevated pressure. The procedure not only was much shorter than a traditional activation process but also increased catalyst utilization dramatically, especially for electrodes with low catalyst loadings. They found that the MEA activation procedure at high temperature and pressure was a quick and effective method for the low temperature PEMFC.

In spite of all these studies, scarce information is provided in the literature regarding the effect of the MEA activation condition on the MEA performance during the activation procedure and after reaching the steady sate condition. The objective of the present study is to compare the effect of MEA activation at low temperature and pressure versus high temperature and pressure on the MEA performance. For this purpose, the MEA performance and EIS response were investigated in details during the MEA activation process and after reaching the steady state condition.

2. Experimental

2.1. MEA fabrication

The anode and cathode catalyst ink was prepared by directly mixing Pt/C 20% wt. (BASF) catalyst with Nafion solution 5% wt. (EW1000, Aldrich). The Nafion content within the catalyst ink was 30% wt. The catalyst ink was sonicated for 30 min in isopropyl alcohol. Then, it was coated onto a gas diffusion medium. The gas diffusion medium consisted of a carbon paper (TGP-0120-Standard Teflon treated, fuel cell store) and diffusion layer containing 20% wt. of Teflon. The prepared composite was dried in an oven at 60 °C for 1 h. The Pt loading was controlled at 0.4 mg cm^{-2}. The resulting composite was divided into four identical gas diffusion electrodes (GDEs) in order to make two identical MEAs. The MEA was prepared by placing two GDEs on both sides of the Nafion 212 membrane.

2.2. MEA testing

All experiments were conducted on a fuel cell test station (Scribner, 850e) with a cell hardware (5 cm^2, AHNS Co.). Both MEAs were activated at 0.6 V according to [14], but were experienced in low and high pressure and temperature during conditioning. One MEA was activated at 55 °C and 34 kPa pressure, assigned as MEA-LTP. Another MEA was activated at 75 °C and 172 kPa pressure of gases, assigned MEA-HTP. In order to attain the stable MEA performance at the given thermal and pressure operating condition, relative humidity (RH) of reactant gases was optimized. Fully humidified gases with flow rate 200 ml min^{-1} were applied for MEA-LTP whiles in the case of MEA-HTP, RH of anode and cathode was kept at 100% and 50%, respectively and flow rates of reactants were 500 ml min^{-1}. To avoid the oxidant or fuel starvation condition, the gases were supplied in excess of the stoichiometric amount for both MEAs.

MEAs activation was interrupted every hour for a set of i-V curve and EIS measurements. After MEA conditioning, the performance and EIS response of both MEAs were investigated under different operation conditions.

Polarization curves were obtained by scanning of the cell voltage from OCV to 250 mV with a scan rate of 5 mV s^{-1}. Impedance spectra were also recorded at 0.5 V over the frequency range from 10 kHz to 10 mHz. The amplitude of the AC signal was kept at 5% of the cell DC current.

All tests were repeated twice and the first forward scan has been reported.

3. Results and discussion

3.1. The performance and EIS evaluation of MEA-LTP and MEA-HTP during activation

Fig. 1a and b present the polarization curves of MEA-LTP and MEA-HTP at different instants: 1, 3, 5, 8 and 9 h along the activation process under the constant voltage of 0.6 V, respectively. The results show that the performance of both MEAs increases over the entire potential range during the time. A significant change in the maximum power density (MPD) occurs for MEA-LTP from 463 mW cm^{-2} at the first hour of activation to 1010 mW cm^{-2} at the last hour, in contrast to 672 mW cm^{-2} to 1110 mW cm^{-2} for MEA-HTP. It means that MEA conditioning at high T and P leads to a higher performance, as compared to MEA conditioning at low T and P. This is also consistent with the results obtained by Z. Qi et al. [19].

In order to analyze the performance of both MEAs, the values of the current density of MEA-LTP and MEA-HTP at 0.8 V, 0.6 V and 0.3 V were plotted and compared, as shown in Fig. 2. It is interesting to note that MEA-HTP achieves the steady state performance after 5 h, as compared to 8 h for MEA-LTP. A lower performance is also obtained by MEA-LTP, which was activated under low T and P. This demonstrates that MEA activation under high temperature and pressure improves the rate of approaching the equilibrium state and reduces the time of MEA activation by at least 40%. At the end of the MEA activation, the current density value at 0.6 V of MEA-HTP is approximately 20% higher than that of MEA-LTP (1620 mA cm^{-2} vs. 1380 mA cm^{-2}).

EIS experiments were also conducted at 1-h intervals during the MEA activation process. Fig. 3a and b depict the impedance spectra for MEA-LTP and MEA-HTP, respectively, at different instants: 1, 3, 5, 8 and 9 h, during the MEA activation. The Nyquist plots of both MEAs consist of two arcs in high and low frequency regions that are associated with the dynamics charge and mass transfer resistances in both MEAs, respectively [21]. As can be seen in Fig. 3, the diameters of high and low frequency arcs in the EIS spectra of both MEAs decrease throughout the activation process, suggesting a reduction in charge and mass transfer resistances.

In the case of MEA-HTP, the large arc in the low frequency region is observed at the end of activation. This can be explained as